

# Temperature-Dependence of Electrical Conductivity for Some Natural Coordination Polymeric Biomaterials Especially Cross-Linked Tetravalent Metal-Alginate Complexes with Correlation between the Coordination Geometry and Complex Stability

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## Abstract

The electrical conductivity ( $\sigma$ ) of some coordination biopolymeric cross-linked zirconium (IV)- and tin (IV)-alginate complexes in the form of circular discs has been measured as a function of temperature. The measured values of the electrical conductivities were found to be in the range of semiconductors. The Arrhenius plots of  $\log \sigma$  vs.  $1/T$  showed a complex behavior where two main conduction regions separated by two transition parabolic zones were observed. The observed increment in  $\sigma$  values at the early stages was explained by formation of free-radical intermediates involving metal ions of lower oxidation states, whereas the sharp increment in  $\sigma$  values at the elevated temperatures was interpreted by the degradation of such intermediates formed to give rise to the metal oxides as final degradation products. The X-ray diffraction patterns indicated that the alginate complexes are amorphous in nature. Infrared absorption spectra revealed a sort of complexation among the polyvalent metal cations and the functional carboxylate and hydroxyl groups of alginate macromolecule. A suitable conduction mechanism was suggested and discussed in terms of the complex stability related to the coordination geometry.

## Keywords

Polymeric Biomaterials, Semiconductors, Algimates, Complexes,

## Geometry

### Introduction

Alginate is a binary linear heteropolymer consisting of 1,4-linked  $\beta$ -D-mannuronic and  $\alpha$ -L-guluronic acids units. The monomers are arranged in a clockwise along the macromolecular chains (Chanda et al.).

Conducting polymers offer the promise of the achievement a new generation of polymers and materials that exhibit a high potential application in technological sensor industry (Nandapure et al.; Kondawar et al.; Jing et al.; Mead; Sulaneck et al.). Conductance measurements of polymers sandwiched between two metal electrodes have attracted much attention owing to their wide applications as sensors in electronic devices (El-Dossouky et al.) as well as to the acquisition of more information on the structure of materials which have been achieved from such electrical conductivity measurements.

Although, conducting polymers in particular that prepared from synthetic polymers have been the subject of continuous research and development in recent years owing to their unique electrical, optical and chemical properties (Abdel-Wahab et al.), a little attention has been focused on that of natural polymers. This fact may be attributed to the lack of information achieved on the electrical properties of

such materials. Even though, Hassan and co-workers investigated the behavior of electrical conductivity of some coordination biopolymeric natural polymers such as cross-linked metal-alginate complexes in either gel or granule forms. For example the electrical conduction as a function of frequency was investigated for coordination biopolymeric metal-alginate complexes biopolymeric in either granule (Abdel-Wahab et al.; Ahmed et al.) or gel (Hassan et al.; Hassan) nature. Again, the electrical conductivities as a function of temperature for such cross-linked complexes of monovalent-(Hassan), divalent (Khairou et al.), trivalent (Zaafarany et al.; Hassan et al.), tetravalent (Zaafarany et al.) and hexavalent (Hassan et al.) metal cations have been studied and reported elsewhere. Unfortunately, the discrepancies and variety of electrical conductivity behavior observed in those studied complexes makes their corresponding conduction mechanisms unclear and incomplete.

In view of the above aspects and our interest on studies of natural polymeric biomaterials, the behavior of electrical conductivities of the present complexes seems to merit an investigation with the aim of shedding more highlights on the conduction mechanism as well as to gain more information on the correlation between the electrical properties in terms of stability and geometrical structure in these coordination polymeric biomaterial complexes.

## Experimental

### Materials

Sodium alginate used was Cica-Reagent (Kanto Chem. Co.). Doubly distilled conductively water was utilized in all preparations. All other materials used were of analytical grade.

### *Preparation Of Tetravalent Metal-Alginate Granules*

Cross-linked metal-alginate granules were prepared by the replacement of  $\text{Na}^+$  counter ions in alginate macromolecule by the corresponding quadrivalent metal cations as described elsewhere (Hassan; Khairou et al.; Zaafarany et al.; Hassan et al.; Awad et al.). This process was performed by stepwise addition of the alginate powder to the electrolyte solutions of metal ions whilst rapidly stirring the solutions to avoid the formation of lumps, which swell with difficulty. After completion of the exchange process, the grains formed were collected and washed several times with deionized water until the resultant water became free from non-chelated metal ions and then dried under

vacuum over anhydrous  $\text{CaCl}_2$  or  $\text{P}_2\text{O}_5$ .

Samples in the form of circular discs with diameter 13 mm and thickness 1-2 mm were obtained using an IR disc press at a constant pressure of 1500 psi.

### *X-ray diffraction*

The X-ray diffraction patterns were obtained using a Philip 1710 diffractometer as described elsewhere (Hassan; Khairou et al.; Zaafarany et al.; Hassan et al.; Awad et al.).

### *IR Spectra*

The IR spectra were scanned on a Pye Unicam Sp 3100 spectrophotometer using the KBr disc technique (4000-400  $\text{cm}^{-1}$ ).

### *Conductance Measurements*

The specific mechanical properties of metal-alginate complexes in the gel form make the measurements of their electrical properties by means of the conventional methods very difficult. Therefore, a new technique of measurements involving a new cell device has been devised in order to overcome the difficulties (Hassan et al.; Hassan).

The dc conductance was measured over the temperature range 290-560 °C using a Keithely 610 C electrometer. The electrodes used were of circular shape forming a M-S-M sandwich, where M represents the electrodes and S is the specimen. The metal-alginate complex discs were sandwiched between the two standard electrodes (graphite, copper or silver paste) mounted into a specially designed temperature-controlled electric furnace provided with a standard copper-constantan thermocouple. The samples were kept short circuited for 3-5 h to make it ready for experiments. The electrical resistance of the samples was measured, and from this the electrical conductivities ( $\sigma$ ) were calculated as follows

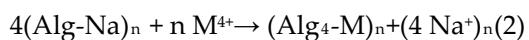
$$\sigma = (1/R)(L/a) \quad (1)$$

where R is the resistance ( $\Omega$ ), a is the area of the sample surface ( $\text{cm}^2$ ) and L is the thickness of the specimen (cm).

## Results and Discussion

Cross-linked tetravalent metal-alginate complexes are formed when the  $\text{Na}^+$  counter ions of alginate macromolecule are replaced by an equivalent amount of tetravalent metal cations. The interdiffused metal ions chelated the carboxylate and hydroxyl functional

groups of alginate macromolecular chains through formation of partially ionic and partially coordinate bonds (Hirst et al.), respectively, and then mediated through blocks of alginate macromolecular chains in an egg-carton like structure (Hirst et al.; Rees et al.; Schweiger). This exchange process occurs inherently and stoichiometrically even the valences and mobilities of the two exchanging counter ions are quite different (Hellferich)



*solid aqueous solid complex aqueous*

where ( $\text{Alg} - \text{Na}$ ), ( $\text{Alg}_4 - \text{M}$ ) and  $\text{M}$  are sodium alginate, metal-alginate complex and the chelated metal ion, respectively.

The X-ray diffraction patterns indicate that the investigated alginate complexes are amorphous in nature. Relevant infrared bands which provide considerable structural evidence for the mode of attachment between these tetravalent metal cations and alginate functional groups are shown in Fig. 1. The vibrational assignments of the bands showed that the bands of  $\nu_{\text{s}}\text{CO}_2^-$  and  $\nu_{\text{as}}\text{CO}_2^-$  are shifted from 1600 and 1400  $\text{cm}^{-1}$  in alginate to higher frequencies of 1634 and 1414  $\text{cm}^{-1}$  in the complexes indicating the

complexation between the interdiffused metal cations and the carboxylate and hydroxyl functional groups of alginate macromolecular chains (Bellamy; Cozzi et al.).

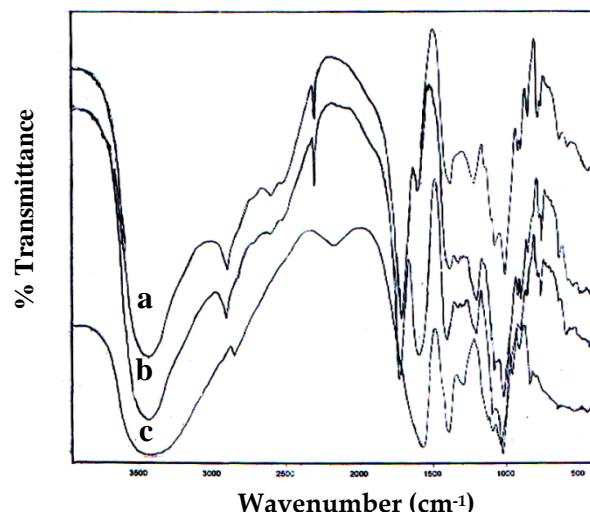


FIG.1 INFRARED SPECTRA OF (A): ZIRCONIUM(IV); (B) : TIN(IV); IN CROSS-LINKED METAL(IV)-ALGINATE COMPLEXES AND (C): ALGINATE SUBSTRATE

The broad band observed at around 3500  $\text{cm}^{-1}$  which belongs to  $\nu_{\text{OH}}$  of water (or OH-free functional groups) is also shifted to lower frequencies as shown in Table 1.

TABLE 1 FTIR FREQUENCIES ( $\text{CM}^{-1}$ ) FOR SODIUM ALGINATE AND SOME CROSS- LINKED METAL-ALGINATE COMPLEXES

Complex	$\nu_{\text{s}}\text{OCO}$	$\nu_{\text{as}}\text{OCO}$	$\nu_{\text{OH}}$	$\nu_{\text{M-O}}$	Reference
Na-alginate	1400	1600	3500	850	Hassan
Ag <sup>I</sup> -alginate	1400	1615	3444	830	Hassan
Sn <sup>IV</sup> -alginate	1414	1634	3457	811	This work
Zr <sup>IV</sup> -alginate	1408	1629	3447	813	This work
Cr <sup>III</sup> -alginate	1420	1637	3463	810	Hassan et al.
Fe <sup>III</sup> -alginate	1418	1633	3448	817	Hassan et al.
La <sup>III</sup> -alginate	1419	1598	3426	820	Zaafarany et al.
Ce <sup>III</sup> -alginate	1421	1618	3441	815	Zaafarany et al.
Th <sup>IV</sup> -alginate	1419	1635	3461	890	Zaafarany et al.
Se <sup>IV</sup> -alginate	1408	1629	3387	806	Zaafarany et al.
U <sup>VI</sup> -alginate	1410	1591	3410	817	Hassan et al.

Notes:  $\nu_{\text{s}}$ : Symmetry stretching vibrations of OCO,  $\nu_{\text{as}}$ : Assymetry stretching vibrations of OCO,  $\nu_{\text{OH}}$  : Stretching vibrations of H bond of OH,  $\nu_{\text{M-O}}$  : Stretching vibrations of metal-oxygen bond

The free-ligand has a strong band at 1735  $\text{cm}^{-1}$  which can be assigned to the carbonyl stretching vibration of the carbonyl group (Cozzi et al.). The displacement of this band at around 1742-1747  $\text{cm}^{-1}$  may also indicate the coordination of the carboxylate groups with the

appearance of both symmetric ( $\nu_{\text{s}}$ ) and asymmetric ( $\nu_{\text{as}}$ ) vibrations of COO<sup>-</sup> group. Again, the location of  $\nu_{\text{s}}$  COO<sup>-</sup> is diagnostic of bridging carboxylate groups. The electrical conductivities of Zr<sup>IV</sup>- and Sn<sup>IV</sup>-alginate complexes in the form of circular discs have been

measured as a function of temperature. As shown in Fig. 2, plots of  $\log \sigma$  against  $1/T$  of Arrhenius equation displayed a complicated behaviour where two distinct conduction zones are observed.

A similar behavior was observed in analogous studies of the temperature-dependence of the electrical conductivity of some other cross-linked metal-alginate complexes (Hassan; Khairou et al.; Zaafarany et al.; Hassan et al.; Awad et al.). The observed increment of the electrical conductivity with the increasing

temperature at the early stages was attributed to the evolution of coordinated water molecules in the amorphous phase by dehydration processes or formation of free-radical substrates in those studied complexes. However, the absence of such parabolic behavior at the early stages of measurements for some other metal alginate complexes despite the presence of coordination water molecules in their amorphous phases (Khairou et al.; Zaafarany et al.) leads to excluding the proposal of evolution of coordinated water molecules.

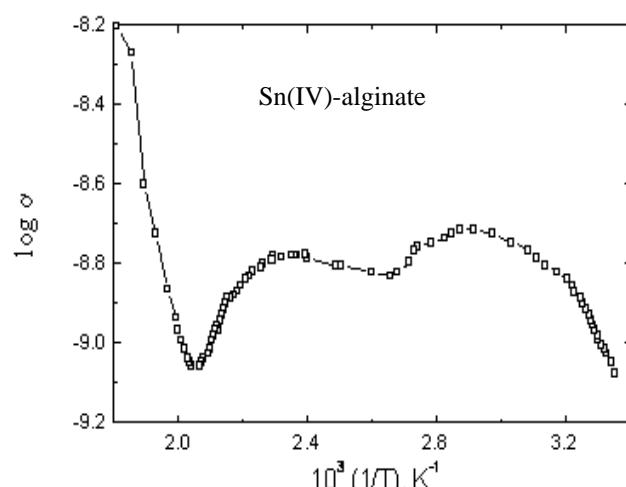
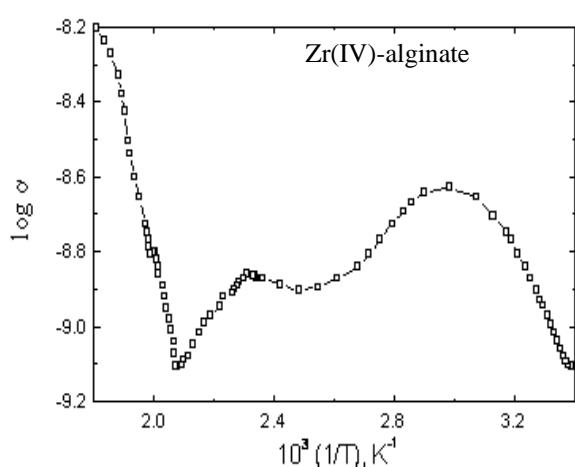


FIG. 2 PLOTS OF LOG  $\sigma$  AGAINST  $1/T$  OF ZIRCONIUM (IV) AND TIN (IV) CROSS-LINKED METAL (IV)-ALGINATE COMPLEXES

Consequently, observed parabolic behavior may be explained by formation of free-radical intermediates involving chelated metal cations of oxidation states lower than that of the original untreated complexes. This suggestion was based on the possibility of transfer of electrons from the alginate macromolecule to the cross-linked metal cations. Hence, the number of transition zones is mainly dependent on the probable oxidation states formed during the reduction of chelated metal cations. For example, chromium (III) and iron (III) are well-known to be of one-equivalent oxidant nature (Cotton et al.), i.e. only  $\text{Cr}^{II}$  and  $\text{Fe}^{II}$  oxidation states are formed on reduction. Therefore, the number of expected transition zones should be only one as experimentally observed (Zaafarany et al.; Hassan et al.). Again, uranium(VI) is a multiequivalent oxidant (Hassan) which gives various oxidation states,  $\text{U}^{IV}$ ,  $\text{U}^{IV}$  and  $\text{U}^{III}$ , respectively, through successive one-electron-transfer mechanism in a sequence on reduction. Therefore, three parabolic shapes should be exhibited as reported earlier (Khairou et al.). On the other hand, divalent- and some trivalent-metal cations such as lanthanum (III) and cerium (III) are difficult to be reduced to lower oxidation states (Cotton et al.).

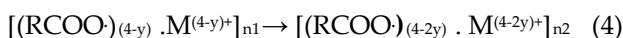
Hence, no formation of transition zones could be expected as reported elsewhere (Zaafarany et al.; Awad et al.).

In view of the above interpretations and the experimental observations, a similar conduction mechanism suggested earlier (Hassan; Zaafarany et al.; Awad et al.), may be followed in the present investigation. Zirconium(IV) and tin(IV) are known to be of two-equivalent nature (Cotton et al.) which in turn should manifest two parabolic zones as shown in Fig. 2. Consequently, the increment in  $\sigma$  values with the increasing temperature at the early stages with respect to the studied complexes can be explained by the transfer of one -electron from alginate macromolecule to the chelated quadrivalent metal cations forming free-radical intermediate substrates and metal cations of lower oxidation states as follows

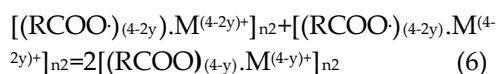


where  $\text{RCOO}^-$  and  $\text{RCOO}\cdot$  refer to the free alginate and its free-radical substrate, respectively, in their complexes, M denotes the chelated metal cations and y is the number of electrons transferred. The observed

increase in the electrical conductivities in the second-stage in these complexes can be interpreted in a similar manner by transfer of a further electron from the alginate to the reduced form of chelated metal ion (Eq. 3), i.e.

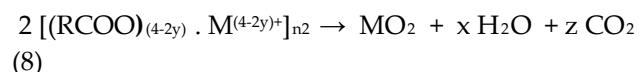
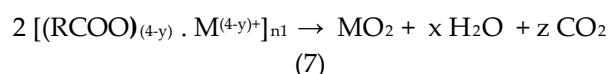


A question of basic interest that may be considered in case of Zr<sup>IV</sup>- and Sn<sup>IV</sup>-alginate complexes is whether these chelated metal cations are reduced by successive one-electron transfer mechanism ( $M^{4+} \rightarrow M^{3+} \rightarrow M^{2+}$ ) in a sequence or through a simultaneous two-electron changes in a single step ( $M^{4+} \rightarrow M^{2+} \rightarrow M^0$ ). The presence of two transition zones (Fig. 2) may indicate the presence of both two mechanisms, but from the thermodynamic and energetic points of view, the former mechanism is the more probable one. It may be noticed that the second transition zone is relatively small compared to the first one. This can be attributed to the extreme instability of the formed intermediates which were rapidly decomposed by degradation resulting in metal oxides as final degradation products (Zaafarany et al.; Said et al.). Of course, the dimerization of the free-radicals will lead to a decrement in the charge carriers and, hence, a decrement in the electrical conductivity should be expected as observed experimentally. This dimerization can be expressed by the following equations



On the other hand, the sharp increase in  $\sigma$  values observed at elevated temperatures can be explained by the degradation of the intermediates to give rise to the

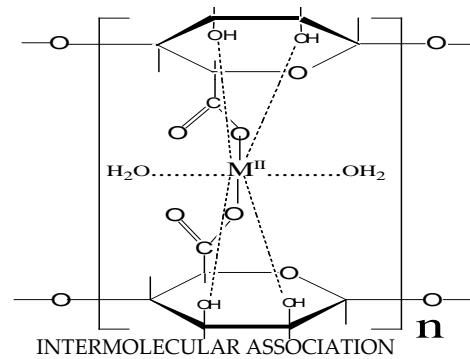
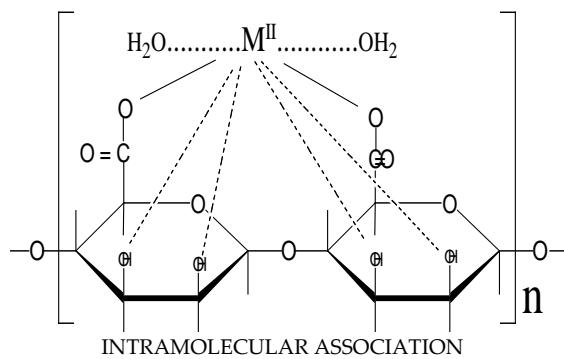
corresponding metal oxides ( $MO_2$ ) as final products (Zaafarany et al.; Said et al.)



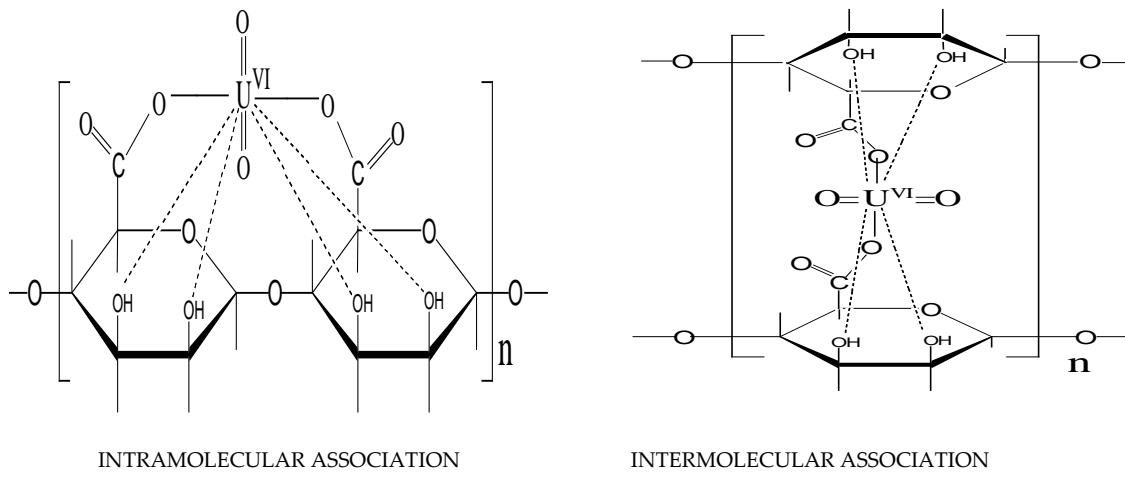
The values of electrical conductivities obtained using different electrodes were found to be in good agreement with each other confirming the reproducibility of the conductance measurements. In other words, it means that the nature of electrodes has no influence on the behavior of electrical conductivity.

It was reported (Hassan; Thomas et al.; Braccini et al.) that the interdiffused metal ions chelate the functional groups of alginate macromolecular chains through two geometrical structures. The first type corresponds to an intramolecular association in which the functional groups involved in chelation belong to the same chain. Hence, the plane involving the chelated metal ions is parallel with that of alginate macromolecular chains. This configuration may be called a planar geometry. The second structure corresponds to the intermolecular association in which the plane containing the metal ions is perpendicular to that of alginate chains. Here, the involved functional groups are related to different chains and the configuration obtained is termed as a non-planar geometry. The type and nature of geometry depend on the valency and the coordination number of chelated metal ion in the complex. Divalent and hexavalent metal cations (Cotton et al.) are known to be of octahedral six coordination geometry in their complexes and, hence, it tends to chelate the functional groups via either inter- or intramolecular association in order to attain the octahedral geometry in their complexes as shown in Schemes I and II.

#### CHELATION IN DIVALENT METAL ION COMPLEXES



SCHEME I



SCHEME II

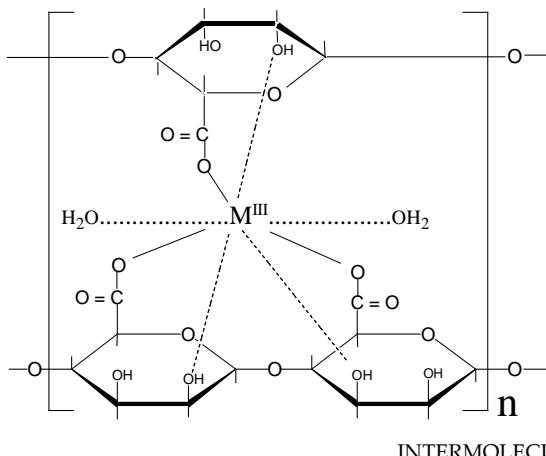
The priority of these two geometrical structures depends on the stability of the complexes formed. In addition, trivalent- and tetravalent-metal ions are enforced to cross-link the functional groups of alginate macromolecule via only intermolecular association in their alginate complexes for geometrical reasons (Scheme III). The preferability of intermolecular association mechanism for chelation in case of the

latter metal-alginate complexes can be explained by their tendency to decrease the bond stretching resulting from the occurrence of metal-oxygen bond elongation in case of intramolecular association (Hassan).

In view of the above interpretation, the geometrical structure in those metal alginate complexes can be

#### CHELATION IN TRIVALENT METAL ION

##### COMPLEXES

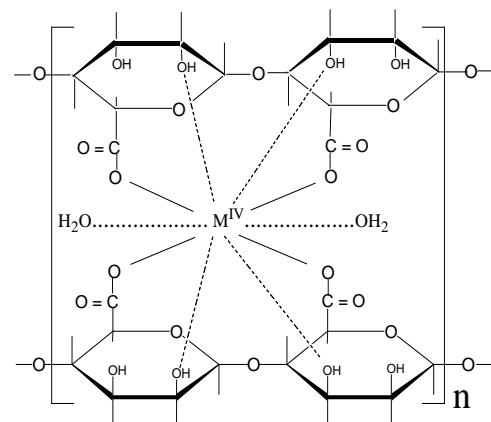


SCHEME III

achieved through chelation of the interdiffused metal ions with the carboxylate groups as principal units in addition to the hydroxyl and/or the water molecules of the amorphous phase. This is to complete the coordination number of the chelated metal ion and react with the complex to a more stable geometry. It is well known that the charge carriers drift their velocity to maximum in case of intermolecular association complexes owing to the presence of channels around the planes containing the metal ions rather than in

#### CHELATION IN TETRAVALENT METAL ION

##### COMPLEXES



case of intramolecular association. Hence, the electrical conductivity is expected to be higher in non-planar than that in planar geometries (Hassan; Thomas et al.; Braccini et al.). As shown in Table 2, the value of electrical conductivity lies in the range of semiconductors for monovalent, trivalent and tetravalent metal-alginate complexes, indicating that the chelation in these metal-alginate complexes should be of intermolecular association geometry which may confirm our suggestion (Scheme III).

TABLE 2 THE ACTIVATION ENERGIES IN EV AND THE ELECTRICAL CONDUCTIVITY IN  $\Omega^{-1} \text{cm}^{-1}$  (290 K) FOR SOME CROSS LINKED METAL-ALGINATE COMPLEXES

Complex	$E_a$ (initial stage)	$E_a$ (final stage)	$\sigma$ ( $\Omega^{-1} \text{cm}^{-1}$ )	Reference
Sn <sup>IV</sup> -alginate	0.33	0.98	1.11x10 <sup>-9</sup>	This work
Zr <sup>IV</sup> -alginate	0.36	0.85	1.16x10 <sup>-9</sup>	This work
Ag <sup>I</sup> -alginate	0.21	3.15	1.8x10 <sup>-8</sup>	Hassan
Cr <sup>III</sup> -alginate	0.16	2.74	10.0x10 <sup>-9</sup>	Hassan et al.
Fe <sup>III</sup> -alginate	0.22	1.41	2.0x10 <sup>-9</sup>	Hassan et al.
La <sup>III</sup> -alginate	-	1.47	1.3x10 <sup>-9</sup>	Zaafarany et al.
Ce <sup>III</sup> -alginate	-	1.19	1.0x10 <sup>-9</sup>	Zaafarany et al.
Th <sup>IV</sup> -alginate	0.86	1.20	2.01 x10 <sup>-9</sup>	Zaafarany et al.
Se <sup>IV</sup> -alginate	0.25	1.17	6.0x10 <sup>-9</sup>	Zaafarany et al.
U <sup>VI</sup> -alginate	0.37	0.83	1.7x10 <sup>-12</sup>	Hassan et al.

On the other hand, the values of the electrical conductivities for uranium (VI)- and silver(I)-alginate complexes listed in Table 2 may indicate that the uranyl ion prefers to coordinate the functional group of alginate macromolecule through intramolecular association mechanism, whereas silver(I) prefers to be chelated through intermolecular association in its alginate complex in a good accord with that reported earlier (Hassan). Generally, the conductance in polymeric compounds occurs via two conduction mechanisms named ionic and electronic conduction, respectively, depending on the nature of the charge carriers existing within the network of the macromolecular chains (Sulaneck et al.). The value of activation energy may be considered as indirect evidence for the conduction mechanism. When the value of the activation energy,  $E_a$ , is larger than unity, it means that the cationic conduction mechanism tends to be the more prominent one, whereas that value is usually lower than unity in case of electronic conduction mechanism. The activation energies in these cross-linked metal alginates can be evaluated from the slopes of  $\log \sigma - 1/T$  plots using the Arrhenius equation

$$\sigma = \sigma^0 \exp(-E_a/RT) \quad (9)$$

where  $\sigma$  is the electrical conductivity,  $\sigma^0$  is a constant and  $E_a$  is the activation energy of the charge carriers. The values calculated by using the least-squares method are summarized along with that of other cross-linked metal alginate complexes in Table 2. The lower values of activation energy less than 1.0 eV observed for studied tetravalent metal alginate complexes in the present work may reflect the prominence of the electronic conduction mechanism. The formation of free-radicals through the treatment of the studied complexes may support this suggestion.

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